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STATISTICAL-MECHANICAL STUDY OF POLYVINYLIDENE FLUORIDE
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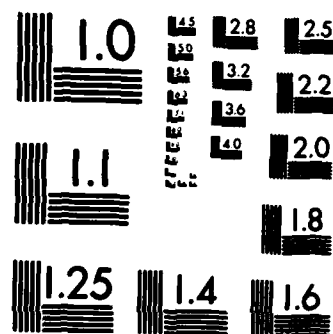
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 17224.6-PH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) STATISTICAL-MECHANICAL STUDY OF POLYVINYLIDENE FLUORIDE		5. TYPE OF REPORT & PERIOD COVERED FINAL-July 1980 - June 1984
7. AUTHOR(s) Philip L. Taylor		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Case Western Reserve University 10900 Euclid Avenue Cleveland, OH 44106		8. CONTRACT OR GRANT NUMBER(s) DAAG-29-80K-0047
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE June 1, 1984
		13. NUMBER OF PAGES
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Piezoelectric, pyroelectric, polymer, ferroelectric, polyvinylidene fluoride		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A final report is presented of work performed in the study of the properties of polyvinylidene fluoride by the theoretical techniques of statistical mechanics and condensed-matter theory. The nature of piezoelectricity and pyroelectricity in polymers and their dependence on crystal structure and internal electric fields has been thoroughly investigated. The time-dependence and microscopic origin of the poling. over...		

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process has been studied and accounted for. The principal results have been described in 16 publications in refereed journals.

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STATISTICAL-MECHANICAL STUDY OF POLYVINYLIDENE FLUORIDE

FINAL REPORT

PHILIP L. TAYLOR

JUNE 1, 1984

U.S. ARMY RESEARCH OFFICE

GRANT NUMBER DAAG-29-80K-0047

CASE WESTERN RESERVE UNIVERSITY

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A. Statement of the Problem Studied

The performed research consisted of a theoretical study of both equilibrium and non-equilibrium properties of poly(vinylidene fluoride), hereafter referred to as PVF_2 . This material can exhibit strong piezoelectric and pyroelectric effects if suitably prepared, and is consequently of great technological interest. The study consisted of a series of calculations of the equation of state, and the mechanism by which electrical activity is induced.

Detailed accounts of the results of our investigations have been given in the papers listed in section C, and so we here just provide a brief summary of some of the more important aspects of our work.

B. Summary of Most Important Results

The thermodynamic response of pyroelectric and piezoelectric materials has been studied, and the relationship found between the forces acting on devices and those on isolated samples of materials. Because polymers typically have low elastic moduli, the secondary pyroelectricity due to changes in sample shape is often important. The relationship between changes in dipole moment of a sample and the traditionally-defined primary and secondary components of pyroelectricity have been defined. This differs from the usual division of pyroelectricity into primary and secondary effects, as the usual definition considers changes in polarization, which is the dipole moment per unit volume, rather than the dipole moment itself. This new approach to the thermodynamics allows some simplifications to be made in the interpretation of experiments, and has lent support to the hypothesis

of Kepler and his co-workers at Sandia that some reversible crystallization is occurring in PVF_2 .

The internal electric fields in polyvinylidene fluoride have been shown to be qualitatively different from previously suggested values. A detailed theory of these fields has now been produced, and is currently being applied. In this work the relationship between dipole field sums and Lorentz tensor components in single crystals has been described, and used to develop a method for computing the tensor components via rapidly convergent sums of Bessel functions. The method was used to compute Lorentz factors for simple, body centered and base centered orthorhombic lattices, and derivatives of Lorentz factors for simple orthorhombic lattices. Both the Lorentz factors and their derivatives were found to be very sensitive to lattice structure. The Lorentz-factor formalism was used to derive the equivalent of the Clausius-Mossotti relation for general orthorhombic lattices, and to relate permanent molecular dipole moment to crystal polarization for the case of a ferroelectric of polarizable point dipoles.

We have also derived expressions for piezoelectric and pyroelectric coefficients for a crystal of polarizable point dipoles. The effect of crystal structure on the local electric field acting to polarize the molecules was included via the Lorentz factor formalism. The derived expressions for the piezo and pyroelectric coefficients were found to contain terms dependent on derivatives of the Lorentz factors. These terms reflect the changing of molecular dipole moments in response to the changing local electric field in the strained crystal. Inclusion of this effect resulted in predictions of coefficients substantially different from those obtained using the customary Lorentz-field approximation.

The dynamics of the process, known as poling, by which piezoelectric activity is induced was also studied theoretically. The very short poling times, of the order of microseconds, predicted by the theory have since been confirmed elsewhere by experiment. These measurements of the high-field ferroelectric switching characteristics involved application of strong electric fields to films of β -PVF₂ and observation of a rapid increase in the electric displacement. We have concluded that the detailed form of this result is consistent with a previously discussed model in which polarization occurs through propagation of solitary waves of rotation along the axis of the polymer chain.

At the time that the theoretical models were formulated, little experimental information existed concerning the rate at which the switching process occurred. It was known, however, that a period of the order of minutes was sufficient to pole a sample by annealing in an appropriately strong electric field. Detailed calculations indicated that no model in which poling occurred through rotation of a chain by 180° about its axis could yield such rapid switching. A model first suggested by Kepler and Anderson, however, in which each chain rotated by only 60°, led to a prediction of poling time of the order of milliseconds or less. The recent experimental work, which showed switching to occur in times of the order of microseconds, thus lends support to the model in which 60°-rotation occurs.

We have further examined this model, in which poling occurs through propagation of a solitary torsional wave of polarization along the polymer

chain. An expression for the expected time variation of the electric polarization has been derived and has been found to be consistent with the experimental data.

C. Publications Supported

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12. J.D. Clark, P.L. Taylor and A.J. Hopfinger, "Longitudinal Polarization of α - PVF_2 by Kink Propagation," J. Appl. Phys., 52, 5903 (1981).

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14. C.K. Purvis and P.L. Taylor, "Piezoelectric and Pyroelectric Coefficients for Ferroelectric Crystals with Polarizable Molecules", Phys. Rev. B. 26, 4564 (1982).

15. J.D. Clark and P.L. Taylor, "Effect of Lamellar Structures on Ferroelectric Switching in Poly(vinylidene Fluoride)", Phys. Rev. Lett. 49, 1532 (1982).

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D. Participating Scientific Personnel

Philip L. Taylor, Professor of Physics and Macromolecular Science

A.J. Hopfinger, Professor of Macromolecular Science

Y.A. Ono, Research Associate

J.D. Clark, Research Associate

R. Al-Jishi, Research Associate

S.K. Tripathy, Graduate Assistant (Ph.D. earned 1980)

B.J. Good, Graduate Assistant (Ph.D. earned 1983)

B. Orchard, Graduate Assistant (M.S. earned 1982)

A. Banerjea, Graduate Assistant (Ph.D. earned 1983)

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